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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Electroluminescent Phosphor and Process for Making Same

We, SYLVANIA ELECTRIC PRODUCTS INC., a corporation organized under the laws of the State of Delaware, United States of America, of 100, W 10th Street, Wilmington, Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to electroluminescent devices and materials and processes for making the same.

In many lighting applications, it is necessary to produce white coloured electroluminescent emission. One known technique for producing white emission is to mix blue-emitting zinc sulphide electroluminescent phosphors and yellow-emitting zinc sulpho-selenide electroluminescent phosphors together in suitable proportions. This mixture, when electrically excited, yields blue and yellow emission having such relative intensities that a composite white light results.

This known teechnique, however, suffers from certain serious limitations. In particular, many critical interactions among the phosphor synthesis parameters are not quantitatively reproducible. As a result, different batches of the same material, when electrically excited, will now emit light of the same shade; i.e. the ranges of spectral emission of different batches will differ one from another. Further, both the efficiency and the brightness of the above described phosphor mixture are low.

There has now been developed a new electroluminescent phosphor which, depending upon its processing, is capable of emitting blue, white or yellow light.

Accordingly, it is an object of the invention to provide a group of electroluminescent phosphors having different spectral ranges of light emission extending over a substantial portion of the entire visible spectral range.

Another object is to provide a new process for producing a blue, white or yellow emitting electroluminescent phosphor.

Still another object is to provide a new electroluminescent phosphor which, when incorporated into an electroluminescent lamp and electrically excited, produces a bright white light with relatively high efficiency.

It is also an object of the invention to provide a white-emitting electroluminescent phosphor mixture having a reproducible range of spectral emission.

A further object is to provide a white-emitting electroluminescent phosphor mixture of enhanced brightness.

Yet another object is to provide a new electroluminescent lamp adapted to emit white light when energized.

In accordance with the principles of the invention, the starting material is a copper-activated, chloride-coactivated cathodoluminescent phosphor of the zinc sulphide type. (This type of phosphor can be composed either of zinc sulphide or zinc-cadmium sulphide.)

This starting material is mixed with zinc sulphate, copper sulphate and optionally a manganese salt. The amounts added, as expressed as a percentage by weight of the starting material, are as follows: zinc sulphate, 5—100%; the copper content of the copper sulphate, 0.1%—10%; and the manganese content of the manganese salt, 0—5%.

This mixture is fired at a temperature of 700°—900° C, and after cooling is washed with an alkali metal cyanide solution to produce the desired electroluminescent phosphor.

When the initial copper addition is low, and no manganese is present, the resultant product is a blue emitting electroluminescent phosphor. As manganese is added within the ranges indicated, the colour spectrum is shifted from blue, to white, to yellow. For a fixed amount

[*Price 4s. 6d.*]

of copper, an increase in the zinc sulphate content (within the ranges indicated) results in a phosphor of increased brightness and efficiency. Further, as the zinc sulphate content is increased, a larger manganese addition is required.

Analysis of the electroluminescent phosphors so produced has showed that the copper content of these phosphors was always about 0.03%—0.05% by weight of the phosphor, regardless of the amount of copper sulphate added in the initial step of the process. Apparently, only a certain proportion of the added copper is incorporated into the base material, the cyanide wash removing all excess copper.

Yellow-emitting and blue-emitting electroluminescent phosphors produced by the above-described process can be mixed together, the mixture being dispersed in dielectric and interposed between the electrodes of an electroluminescent lamp. When a voltage is supplied to such a lamp, it has been found that a bright white light is produced at relatively high efficiencies. Further it has been found that, while the shade of the white light can be varied by varying the relative proportions of the phosphor components, any particular shade could be reproduced from different batches of phosphors and phosphor mixtures, merely by holding the relative proportions of the two components constant at some predetermined values.

Illustrative embodiments of the invention will now be described in more detail with reference to the examples which follow.

EXAMPLE I

20 grams of a copper-activated, chloride-coactivated cathodoluminescent zinc sulphide phosphor (i.e. cadmium-free phosphor activated with 0.01%—0.03% copper and commercially designated as a Type P-2 phosphor) was blended with 0.5 grams of copper sulphate (a 1% addition of copper), 7 grams of zinc sulphate (35% by weight of the phosphor) and 0.21 grams of manganese carbonate (a 0.5% addition of manganese). The mixture was loaded into a covered quartz crucible which, in turn, was placed in a muffle furnace and fired at a temperature of 800° C for a period of 40 minutes. The crucible was then removed from the furnace and permitted to cool to room temperature.

The fired mixture was then removed from the crucible, washed first with 30-ml. of warm acetic acid (50% concentration) and thereafter washed successively with three separate 30-ml portions of warm distilled water.

Finally, the mixture was washed with a 30-ml portion of a hot solution of potassium cyanide (5% concentration). Thereafter, the material was washed with water, heated to dryness at a temperature of 130° C and sieved through a 325 mesh screen.

The product was incorporated into a 5 mil. gap. 1 inch×1 inch, demountable electroluminescence test cell, using castor oil as a dielectric with a loading of 2 parts by weight of phosphor to 1 part by weight of castor oil. Alternating voltages ranging in value from 100 to 600 volts r.m.s. and ranging in frequency from 60 to 400 cycles per second were applied to the cell. White electroluminescent emission ensued. The shade of the white emission ranged from a warm (incandescent) white at the lower voltages and frequencies to a cool (daylight) white at the higher voltages and frequencies. At a voltage of 600 volts rms and a frequency of 60 cycles per second, the brightness of the cell was found to be about 2 foot lamberts, the cell efficiency being about 2—3 lumens per watt.

The above process was repeated using various percentage additions of zinc sulphate. As the addition was decreased from 35% down to about 5%, the brightness and efficiency of the cell decreased. The 5% addition appeared to be the approximate lower limit for useful brightness and efficiency.

Further, as the zinc sulphate addition was increased toward 100%, it was found that higher manganese additions were required to produce equivalent cell brightness and efficiency, the manganese addition for the 100% zinc sulphate addition being about 1.5%.

It was found that the firing temperature could be varied from 700° C—900° C without adverse effects.

EXAMPLE II

The process set forth in Example I was repeated but with no manganese addition. A blue emitting electroluminescent phosphor was produced.

EXAMPLE III

The process set forth in Example I was repeated, using a 5% manganese addition. A yellow emitting electroluminescent phosphor was produced.

We have found that zinc-cadmium sulphide cathodoluminescent phosphors can be used in any of the foregoing examples as long as these cadmium-containing phosphors are finely ground, as for example by ball milling, prior to mixing the various additives therewith.

Further we found that for any emitted colour, decreasing the copper sulphate addition from about 1% by weight of copper to a minimum of about 0.1% by weight, changed the shade of the emitted colour as, for example, from white to pinkish white. Similarly, increasing the copper addition from about 1% to a maximum of about 10% again

changed the shade of the emitted colour, as for example from white to a cream white.

EXAMPLE IV

20 grams of a copper-activated, chloride-coactivated zinc sulphide cathodoluminescent phosphor were mixed with 0.5 grams of copper sulphate and 7.0 grams of zinc sulphate. This mixture was fired and then washed with cyanide in the manner set forth in Example I to produce a blue-emitting electroluminescent phosphor.

20 grams of the above-identified cathodoluminescent phosphor were mixed with 0.5 grams of copper sulphate, 7.0 grams of zinc sulphate, and 0.84 grams of manganous carbonate (a 2% addition by weight of the phosphor). This mixture was fired to a temperature of 800° C and then washed with cyanide ion to remove all excess copper in the same manner as indicated above to produce a yellow-emitting electroluminescent phosphor.

The two electroluminescent phosphors were mixed together in a ratio of two parts by weight of the blue-emitting electroluminescent phosphor to three parts by weight of the yellow-emitting electroluminescent phosphor.

This phosphor mixture was incorporated into a 5 mil. gap demountable electroluminescence test cell using a castor oil as a dielectric with a loading of two parts by weight of the mixture to one part by weight of the castor oil.

When an alternating voltage of 600 volts rms at a frequency of 60 cycles per second was applied to the cell, white light was emitted. The brightness of the emitted light was about 3.5 foot lamberts, and the efficiency of the cell ranged between 3—5 lumens per watt.

EXAMPLE V

The process of Example IV was repeated using a phosphor mixture ratio of one part by weight of the blue-emitting phosphor to one part by weight of the yellow-emitting phosphor.

As before, white light was emitted, the shade of this white being somewhat "cooler" than that of Example IV.

EXAMPLE VI

The process of Example IV was repeated using a phosphor mixture ratio of one part by weight of the blue-emitting phosphor to three parts by weight of the yellow-emitting phosphor.

As before, white light was emitted, the shade of this white being somewhat "softer" than that of Example IV.

WHAT WE CLAIM IS:—

1. A process for preparing an electroluminescent phosphor from a copper-activated, chloride-coactivated cathodoluminescent phosphor of the zinc sulphide type, the process comprising the steps of mixing the cathodoluminescent phosphor with copper sulphate, zinc sulphate and optionally a manganese salt, the amount of copper added, expressed as a percentage by weight of the cathodoluminescent phosphor, falling within the range 0.1%—10%, the amount of manganese added falling within the range 0—5%, and the amount of zinc sulphate added falling within the range 5%—100%; firing the mixture at a temperature falling within the range of 700°—900° C; and washing the fired mixture with an alkali metal cyanide solution to remove all excess copper therefrom, thus producing the said electroluminescent phosphor.

2. A process according to claim 1 for preparing a white-emitting electroluminescent phosphor, wherein the amount of copper added is about 1%, the amount of manganese added is about 0.5%, and the amount of zinc sulphate added is about 35%.

3. A process according to claim 1 for preparing a blue-emitting electroluminescent phosphor, wherein the cathodoluminescent phosphor is mixed with copper sulphate and zinc sulphate only, the amount of copper added falling within the range 0.1%—10%, and the amount of zinc sulphate added falling within the range 5%—100%.

4. A process according to claim 1 for preparing a yellow-emitting electroluminescent phosphor, wherein the amount of copper added is about 1%, the amount of manganese added is about 5%, the amount of zinc sulphate added is about 35%.

5. A process for preparing an electroluminescent phosphor substantially as described in any one of Examples I to IV.

6. An electroluminescent phosphor prepared by a process according to any one of claims 1 to 5.

7. An electroluminescent lamp including an electroluminescent layer consisting of an electroluminescent phosphor mixture dispersed in a dielectric, the mixture containing a blue-emitting, copper activated electroluminescent phosphor component and a yellow-emitting, copper and manganese-activated electroluminescent phosphor component, both components being phosphors prepared by a process according to claim 1.

8. An electroluminescent lamp according to claim 7 wherein the ratio by weight of the blue component to the yellow component falls within the range 1:3 to 1:1.

9. An electroluminescent phosphor mixture, which when subjected to the influence of an electric field, will produce white light, said mixture comprising a blue-emitting, copper-activated electroluminescent phosphor component and a yellow-emitting, copper- and manganese-activated electroluminescent phosphor component, both components being phos-

phors prepared by a process according to claim 1.

10. An electroluminescent phosphor mixture according to claim 8, wherein the ratio by weight of said blue component to said yellow component falls within the range 1:3 to 1:1.

11. An electroluminescent phosphor mixture substantially as described in Examples IV to VI.

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